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Phenyl Transfer from Silicon to Platinum via the Ortho Metalation of a Phenylsilyl Ligand

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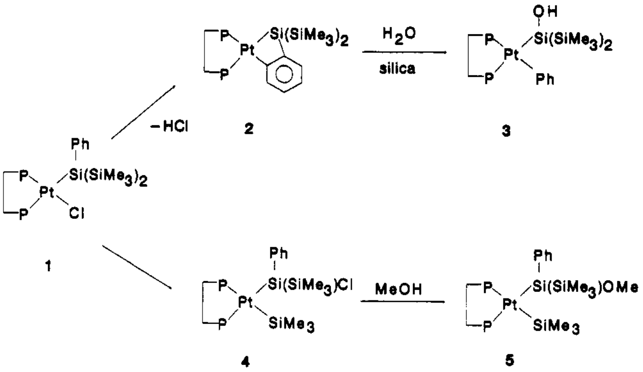
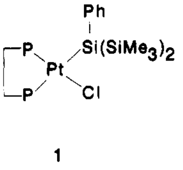
Summary: The first isolated complex resulting from the ortho metalation of an arylsilyl ligand is reported. Thermolysis of the polysilylplatinum complex **1** in benzene-MeOH gives the cyclometalated species **2**. Complex **2** is readily cleaved by water on silica to give the novel platinum compound **3** with a Pt-Ph bond and a silanol moiety on the polysilyl ligand.

Scheme I. Thermolysis of 1 in Refluxing MeOH-Benzene (1:8)



There has been recent interest in silylmetal complexes with respect to the dehydrogenative coupling of hydridosilanes to afford polysilane oligomers and polymers.[1] Many of the known metal catalysts for these reactions also mediate the redistribution of substituents on silicon.[2] In the case of late-transition-metal catalysts, the redistribution of aryl groups is a common occurrence.[3] A likely step in this process is the transfer of an aryl group from silicon to the metal to form a metal aryl species.[4] We now report the transfer of a phenyl group from silicon to platinum in the polysilyl complex 1. The phenyl group transfer proceeds through the novel ortho-metalated complex 2, which readily protodesilylates to give the platinum aryl species 3.



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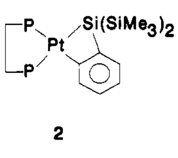

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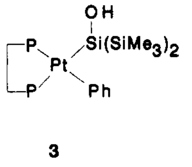

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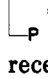

= bis(dicyclohexylphosphino)ethane ; dcpe

We have recently shown that the polysilyl complex 1 isomerizes in refluxing benzene to give the new complex 4 (Scheme I).[5] This complex arises from the interchange of trimethylsilyl and chlorine groups across the platinum-silicon bond. However, thermolysis of 1 in a refluxing mixture of methanol in benzene (1:8) results in ortho

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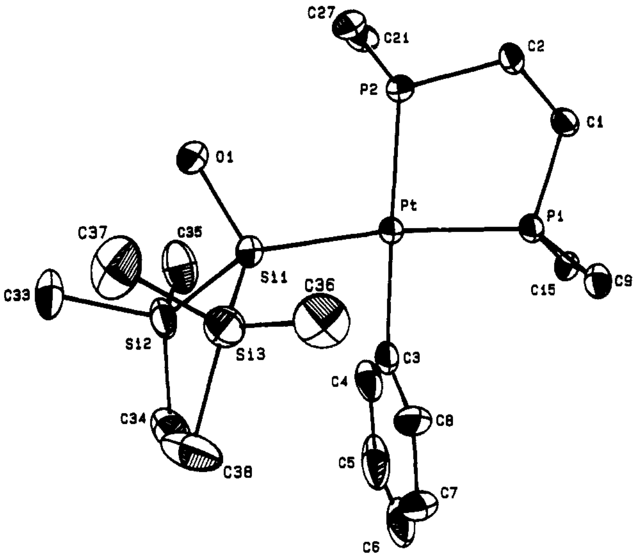

Figure 1. ORTEP diagram of 3 showing non-hydrogen atoms. The nonpendant carbons of the cyclohexane rings have been removed for clarity. Thermal ellipsoids are at the 25% probability level. Selected bond distances (Å) and angles (deg): Pt-Si1, 2.360 (2); Pt-C3, 2.069 (7); Pt-P1, 2.333 (1); Pt-P2, 2.282 (1); Si1-Si2, 2.370 (3); Si1-Si3, 2.380 (3); Si1-O1, 1.726 (4); P1-Pt-P2, 86.50 (5); P1-Pt-C3, 91.3 (1); P2-Pt-Si1, 99.88 (5); Si1-Pt-C3, 82.7 (2); Si2-Si1-Si3, 106.0 (1); Pt-Si1-O1, 113.9 (2).

metalation as the major pathway, giving the cyclometalated derivative 2 in 75% yield. A small amount of the methoxysilyl complex 5, arising from the methanolysis of 4, is also formed (25% yield). The formation of the cyclometalated adduct 2 in methanol-benzene solutions, but not in pure benzene, is consistent with previous studies in which traces of alcohols accelerate the ortho metalation of (arylphosphine)platinum complexes.[6]

Attempts to purify complex 2 by column chromatography (silica; eluent CH_2Cl_2-hexane (1:4)) results in its quantitative conversion into the new complex 3, which is distinguished by a platinum-phenyl bond and a silanol functionality on the polysilane ligand. The ^1J(Pt-P) coupling constants of 1313 and 1922 Hz, as determined by ^{31}P NMR spectroscopy, are consistent with trans aryl and silyl groups, respectively.[7] A sharp O-H stretching vibration at 3640 cm^{-1} suggests little hydrogen bonding in solution.

An X-ray structure determination for 3 was undertaken.[8] An ORTEP drawing of 3 with selected bond lengths and angles is shown in Figure 1. In this complex, the phenyl ring is canted 88° with respect to the square plane of the platinum. The Si-O bond of the silyl substituent lies nearly in the square plane (P2-Pt-Si1-O1 torsion angle 5.6 (3)°) and is directed away from the phenyl group.[9] The Pt-Si bond length of 2.360 (2) Å is slightly longer than those for many mononuclear platinum complexes with sterically nondemanding ligands[10] but is considerably shorter than the previously determined bond lengths of complexes containing the dcpe ligand: 2.423 (2) Å for 1 and 2.389 (1) Å for (dcpe)Pt[Si(SiMe$_3$)$_2$H]Br.[5,11] The Si-O bond length of 1.726 (4) Å is also significantly longer than a typical Si-O bond (1.64 Å).[12,13] The combination of short Pt-Si and long Si-O bond lengths in 3 may originate in part from either π or σ effects. A more efficient back-bonding of the platinum relative to the oxygen for low-lying orbitals on the silicon (π effect) would give short Pt-Si distances and longer than usual Si-O bonds. The same trend in observed bond distances is also reconciled with arguments based on isovalent hybridization[14] which would require greater p orbital participation in the silicon hybrid orbital to oxygen and enhanced s orbital contribution in bonding to the electron-rich platinum (σ effect).

The cyclometalated complex 2 may be isolated in pure form by recrystallization from benzene-hexane solutions. All spectroscopic data are consistent with the proposed structure.[15] The ^1J(Pt-P) coupling constants of 1289 and 1922 Hz are similar to those observed for complex 4, clearly indicating the presence of both aromatic and silyl substituents on the platinum. To our knowledge, complex 2 is the *first* example of an isolated adduct resulting from the ortho metalation of an arylsilyl ligand. This is in contrast with the well known ortho metalations of isoelectronic arylphosphines. The similar covalent radii of silicon and phosphorus (1.18 Å for Si and 1.10 Å for P)[16] suggest that intrinsic structural differences between phosphorus and silicon do not fully account for the difference in reactivity and perhaps some electronic effect is operative. However, the scarcity of known arylsilyl complexes relative to analogous arylphosphine complexes makes any generalization difficult at this time. In the particular case of polysilyl complex 1, ortho metalation may be promoted by steric acceleration due to the relative disposition of the large dcpe and bis(trimethylsilyl)phenylsilyl ligands.[17] The large substituents on platinum and silicon may additionally provide some kinetic stabilization to the product that is formed.

The susceptibility of the cyclometalated complex 2 toward protodesilylation by water on silica suggests that the four-membered ring of this compound is quite labile. Similar facile hydrolysis of the Si-C bond has been observed in strained three- and four-membered-ring systems containing silicon.[18] The selective cleavage of the Si-C

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(7) Characterization for 3: mp 189 °C dec; ^{1}H NMR (δ, C_6D_6) 0.34 (s, 18 H, SiMe$_3$), 0.90-2.60 (m, 49 H, dcpe, Si-OH), 6.90-7.95 (m, 5 H, Ph); $^{31}P\{^1H\}$ NMR (δ, C_6D_6) 61.19 (^1J(P-Pt) = 1313 Hz), 70.36 (^1J(P-Pt) = 1922 Hz); $^{29}Si\{^1H\}$ NMR (δ, C_6D_6) -12.18 (^1J(Si-Pt) = 85 Hz, ^3J(Si-P$_{trans}$) = 8 Hz), 30.88 (^1J(Si-Pt) = 1222 Hz, ^2J(Si-P$_{cis}$) = 7 Hz, ^2J(Si-P$_{trans}$) = 179 Hz); FAB-MS (m/e, NBA matrix) M$^+$, 885 (7%). Anal. Calcd For $C_{38}H_{72}OP_2PtSi_3$: C, 51.50; H, 8.19. Found: C, 51.35; H, 8.07.

(8) Crystal data: dimensions 0.51 × 0.48 × 0.45 mm; crystal system monoclinic; space group $P2_1/c$; $a = 19.756$ (3) Å, $b = 16.909$ (3) Å, $c = 13.031$ (4) Å, $\beta = 95.59$ (2)°; $Z = 4$; absorption coefficient 34.5 cm^{-1}; Mo Kα radiation with graphite monochromator; 2θ range 1.0-48°; 6793 unique reflections with 4998 $\geq 3\sigma(I)$; no absorption correction applied. The structure solution was obtained by direct methods and refined to convergence with full-matrix least squares: $R = 0.041$, $R_w = 0.056$.

(9) The complementary torsion angle C3-Pt-Si1-O1 is -172.1 (3)°; O1 lies 0.013 (6) Å above the mean plane defined by P1, P2, Pt, C3, and Si1.

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(15) Characterization for 2: mp 190-192 °C; ^{1}H NMR (δ, CD_2Cl_2) 0.00 (s, 18 H, SiMe$_3$), 0.95-2.45 (m, dcpe, 48 H), 6.60-7.65 (m, 4 H, Ph); $^{31}P\{^1H\}$ NMR (δ, C_6D_6) 59.39 (^1J(P-Pt) = 1289 Hz), 68.36 (^1J(P-Pt) = 1922 Hz); $^{29}Si\{^1H\}$ NMR (δ, C_6D_6) -12.85 (^2J(Si-Pt) = 86 Hz, ^3J(Si-P$_{trans}$) = 8 Hz), 36.47 (^1J(Si-Pt) = 1246 Hz, ^2J(Si-P$_{cis}$) = 5 Hz, ^2J(Si-P$_{trans}$) = 183 Hz); FAB-MS (m/e, NBA matrix) M$^+$, 867 (3%). Anal. Calcd for $C_{38}H_{70}P_2PtSi_3$: C, 52.57; H, 8.13. Found: C, 50.23; H, 8.00.

(16) Huheey, J. E. *Inorganic Chemistry*: *Principles of Structure and Reactivity*, 3rd ed.; Harper and Row: New York, 1983.

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bond in cyclometalated adducts may provide an essential step in which phenyl groups are transferred from silicon to platinum and, therefore, play a role in certain catalytic redistributions involving arylsilanes. Studies are currently underway to explore this possibility.

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Supplementary Material Available: Complete tables of experimental crystallographic data, positional parameters, bond lengths and angles, root-mean-square amplitudes of anisotropic displacement, torsion angles, and least-squares planes for 3 (17 pages); a listing of structure factors for 3 (50 pages). Ordering information is given on any current masthead page.

Synthesis and Properties of (π-Allyl)palladium Formates as Intermediates in Palladium-Catalyzed Reductive Cleavage of Allylic Acetates and Carbonates with Formic Acid

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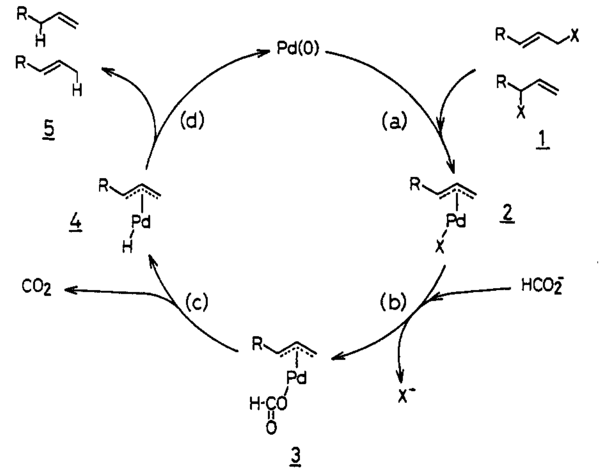
Summary: Neutral (π-allyl)(tertiary phosphine)palladium formates and ionic (π-allyl)bis(tertiary phosphine)palladium formates that are regarded as key intermediates in palladium-catalyzed reductive cleavage of allylic acetates and carbonates with formic acid have been prepared and characterized by ^1H and ^{13}C NMR spectroscopy. From a study of the formation process of these formate intermediates by anion exchange of the acetate anion with formic acid and by establishment of the course of liberation of olefins and CO_2 from the formate ligand, the validity of the proposed catalytic cycle has been substantiated.

Palladium-catalyzed reductive cleavage of allylic compounds, particularly acetates and carbonates, with formic acid provides a convenient synthetic means for regiospecific preparation of terminal olefins.[2,3] The catalytic cycle shown in Scheme I reasonably accounts for the course of the reductive-cleavage process. The cycle is constituted of (a) oxidative addition of the allylic substrate 1 to Pd(0) to give the allylic palladium acetate or carbonate 2, (b) exchange of the anionic group with the formate group to give the allylic palladium formate 3, (c) decarboxylation of the formate ligand to produce the allylic palladium hydride 4, and (d) reductive elimination of the allylic and hydride ligands to liberate the olefin 5 with generation of the palladium(0) species that carries the catalytic cycle.

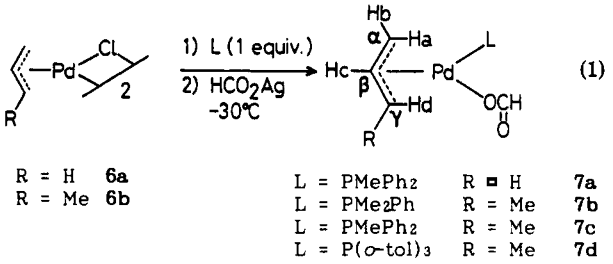
In the catalytic cycle the oxidative addition of allylic acetates is a well-established process.[4,5] Ready oxidative addition of the allylic carbonates to give a (π-allyl)palladium complex having two tertiary phosphine ligands and an ionic carbonate group also has been recently confirmed.[6] However, no study has been made on the preparation and characterization of the putative (π-allyl)palladium formates 3, which serve as key intermediates in the reductive

Scheme I[a]



[a] X = OAc, OCO_2R, OPh, NO_2, etc. Supporting ligand(s) are omitted.

Scheme II



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